Features of the hyperfine field at the nucleus of the ion $^{57}Fe^{2+}$ in antiferromagnetic $CoCO_3$

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(Submitted 9 February 1983)

Pis'ma Zh. Eksp. Teor. Fiz. **37**, No. 9, 417–419 (5 May 1983)

It is shown that the hyperfine field H_{hf} at the nucleus of the ion $^{57}Fe^{2+}$ in $CoCO_3$ is anomalously small but grows rapidly in an external field which lifts the reduction of the electron spin. A study is made of the temperature dependence of H_{hf} and of the NMR gain.

PACS numbers: 76.60.Jx, 75.50.Ee

The impurity ion Fe^{2+} in the "easy-plane" type antiferromagnet $CoCO_3$ has several unusual properties, most notably a low natural excitation frequency $\omega_0 \simeq 1.5\ \text{cm}^{-1}$ (Refs. 1 and 2). It has been shown[3] that the features of this impurity center are due to the orbital degeneracy of the ground state of the Fe^{2+} ion in the crystal field of $CoCO_3$. The projection of the impurity spin on the basal plane is anomalously small, i.e., the spin is "almost orthogonal" to the antiferromagnetism vector **l** of the matrix. We shall show that for "orthogonal" impurities such as this the hyperfine field $\mathbf{H}_{hf}$ at the impurity nucleus typically exhibits unusual behavior, and, consequently, so do the NMR frequency ω_n, the Mössbauer splitting, etc. In particular, the magnitude of H_{hf} is anomalously small and can vary strongly in a weak external magnetic field. At the same time, despite the small value of ω_n, the NMR gain η is anomalously large. Furthermore, the temperature dependence of ω_n and η differ from the usual Brillouin behavior.

Taking into account the specific electronic structure of the ion in question, we can write for $\mathbf{H}_{hf}$ at the ^{57}Fe nucleus an expression of the form[4,5]

$$\mathbf{H}_{hf} = \frac{1}{2} H_c \mathbf{S} - 2\mu_B < r^{-3} > [\, \mathbf{L} - \frac{l(l+1)\mathbf{S} - 3(\mathbf{S}\cdot\mathbf{L})\mathbf{L}}{2(2l+3)(2l-1)}\,], \tag{1}$$

where H_c is the contact field, **S** is the spin of the $3d^6$ shell ($S = 2$), $l = 2$, and **L** is the reduced orbital angular momentum of Fe^{2+} in the cubic field ($L = 1$). By virtue of the relative size of the trigonal-field parameter $\zeta = 1500\ \text{cm}^{-1}$ of the CO_3^{2-} ligands and the spin-orbit-interaction parameter $\lambda = 105\ \text{cm}^{-1}$ of Fe^{2+} (Ref. 6), one need consider only the lowest spin-orbit doublet ($S^z = \pm 2$, $L^z = \mp 1$), which is split in the exchange field Js (s is the average spin of the matrix) by an amount[3] $\omega_0 = 12J^2s^2/\zeta$. In this basis, after expanding in the small parameters λ/ζ, Js/λ, we obtain

$$S^z = (4 - O(J^2s^2/\lambda^2))\sigma^x, \quad L^z = -(2 - O(J^2s^2/\lambda^2))\sigma^x,$$

$$S^x = 2Js\left(\frac{1}{\lambda} + \frac{1}{\zeta}\right) + \frac{2\omega_0}{Js}\sigma^z, L^x = -\left(\frac{9Js\lambda}{\zeta^2} + \frac{3\lambda^2}{2\zeta^2}\right) - \left[4\left(\frac{Js}{\zeta} + \frac{Js\lambda}{\zeta^2}\right) + \frac{3\lambda^2}{\zeta^2}\right]\sigma^z, \tag{2}$$

where σ^i are the Pauli matrices, and $\mathbf{e}_z \| C_3$, $\mathbf{e}_x \| \mathbf{l}$. As a result, Eq. (1) becomes

$$\mathbf{H}_{\rm hf} = (H_{1x} + 2H_{2x}\sigma^z)\,\mathbf{e}_x + 2H_z\,\sigma^x\mathbf{e}_z\ . \qquad (3)$$

Adopting for the sake of definiteness the values $H_c = -500$ kOe and $\langle r^{-3}\rangle = 4.78$ a.u., which account for the observed[5] value $H_{\rm hf} = 184$ kOe in $FeCO_3$, we obtain $H_z \simeq 180$ kOe, $H_{1x} \simeq -39$ kOe, and $H_{2x} \simeq -4$ kOe. If the average relaxation time for an electronic transition is $\tau \ll \omega_n^{-1}$, the hyperfine splitting is determined by the quantity

$$H_{\rm hf} = |\langle \mathbf{H}_{\rm hf}\rangle| = [(H_{1x} + 2H_{2x}\langle\sigma^z\rangle)^2 + 4H_z^2\langle\sigma^x\rangle^2]^{1/2}.$$

In an external field $\mathbf{h} \neq 0$ we have

$$\langle\sigma^{x,z}\rangle = [h_{z,0}/2(h_z^2 + h_0^2)^{1/2}]\,{\rm th}[\omega_0(\mathbf{h})/2T],$$

$$\omega_0^2(\mathbf{h}) = \omega_0^2 + (\mu_B g^{\|}_{\rm ort} h_z)^2,\ g^{\|}_{\rm ort} \approx 6.63\ ^2, \qquad (4)$$

$$h_0 = \omega_0/\mu_B g^{\|}_{\rm ort} \approx 4.8\ {\rm kOe}$$

As one can see from (3) and (4), at $T = 0$ the hyperfine field $H_{\rm hf}$ increases with h_z, from $H_{1x} + H_{2x} \simeq 43$ kOe at $h_z = 0$ to values $\sim (H_{1x}^2 + H_z^2)^{1/2} = 184$ kOe ($H_{\rm hf}$ has increased by a factor of two at $h_z = \sqrt{3}h_0 H_{1x}/H_z$). With increasing temperature, $H_{\rm hf}$ falls rapidly [at $T \sim \omega_0(h)$] to H_{1x} and then decreases more slowly, as the magnetization of the matrix (since $H_{1x} \sim s$). The size of the drop is 4 kOe for $h_z = 0$ and increases rapidly with h_z. The temperature dependence of $H_{\rm hf}$ at various values of h_z is shown in Fig. 1.

As we know, the intensity of the NMR line is governed by the absorption of the matrix at the frequency ω_n. Let us write the expression for the square of the gain

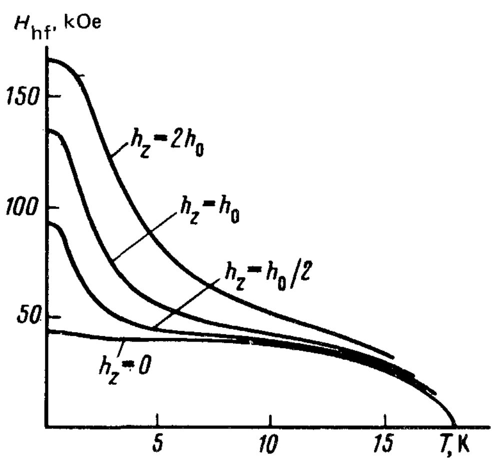

FIG. 1.

coefficient at $h_z = 0$ in an alternating field $\mathbf{h}_\omega \| \mathbf{e}_x$

$$\eta_x^2 = 4\sin^2\frac{\alpha}{2}(u_{10}+v_{10})^4 \langle\sigma^z\rangle^2 \frac{\mu_B^2 g_\perp^2 H_z^2}{\omega_{10}^2}, \tag{5}$$

where α is the angle between the sublattices of the matrix, $u_{1\mathbf{k}}$ and $v_{1\mathbf{k}}$ are the coefficients of a u-v transformations, $\omega_{1\mathbf{k}}$ is the magnon frequency on the lowest branch, and $g_\perp$ is the g factor of the Co^{2+} ion in the basal plane. Using the expression $\omega_{10} = \mu_B \tilde{g}\sqrt{h_y h_D}$ (h_D is the Dzyaloshinskiĭ field), we express $\eta_x{}^2$ in terms of measurable quantities:

$$\eta_x^2 = \frac{\langle\sigma^z\rangle^2}{s^2}\left(\frac{\chi_\perp}{\chi_\|}\right)^2\left(\frac{g_\|}{\tilde{g}}\right)^4\left(\frac{H_z}{h_y}\right)^2, \tag{6}$$

where $\chi_\perp$ and $\chi_\|$ are the susceptibilities of the matrix. Thus the gain coefficient for $T < \omega_0$ is governed mainly by the factor H_z/h_y, which greatly exceed the usual phenomenological value $\omega_n/2\mu_I h_y = H_{\mathrm{hf}}/h_y$. As T increases, the coefficient η_x falls off asymptotically to the phenomenological value $\sim H_{1x}/h_y$. In addition, η_x falls off with increasing h_z, as is dictated by the factor $\langle\sigma^z\rangle\langle H_{\mathrm{hf}}{}^x\rangle/H_{\mathrm{hf}}$.

We remark in closing that the results of this paper admit a simple experimental check.

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Translated by Steve Torstveit
Edited by S. J. Amoretty